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The NKS-NORCMASS guide to beginners in ICP-MS

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Abstract

This text is meant as a guide for those who wishes to approach the field of ICP mass spectrometry for one purpose or another. In principle any mass spectrometer consists of three parts: An ion source, a mass analyser and a detector. These three parts will be treated separately in the text before focusing on the specific issues concerning ultra trace measurements and isotope ratios of radioisotopes. The text includes some general considerations with practical tips which are useful to the novel user when doing sample analysis with ICP-MS. It also includes a short training course consisting of five exercises.

Key words

ICP-MS, Mass spectrometry, training course, isotope ratio measurements

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The NKS-NORCMASS guide to beginners in ICP-MS

This text is meant as a guide for those who wishes to approach the field of mass spectrometry for one purpose or another. Even though there are several types of mass spectrometers installed in the Nordic countries the most common type is ICP instruments and this is the type which is described here. Comparisons to other type of instruments will appear when relevant. The text is in any way not intended to be a full description of this very comprehensive field

In principle any mass spectrometer consists of three parts: An ion source, a mass analyser and a detector. These three parts will be treated separately below before focusing on the specific issues concerning ultra trace measurements and isotope ratios of radioisotopes. In general the sample introduction system with the ion source is the most important component when it comes to sensitivity in transmission, precision and interferences. Although the mass analyser and detection system also are of importance in this respect but the possibility of making changes in the hardware is much more limited and even if possible it seldom makes the same impact as if changes are made in the sample introduction/ion source system.

The ion source

Since the fundamental properties of the mass analyser is to sort ions, that is charged particles, by magnetic and/or electrostatic elements it is necessary to first transform the sample atoms into ions. This can be done in a variety of ways, for instance thermally, by using lasers or in a plasma just to mention a few. The ion source is a very important part of a mass spectrometer. Ideally it should be capable of transforming 100% of the sample atoms into ions all having the same charge and kinetic energy. With ions all having the same initial charge and kinetic energy it would be a rather simple task for the mass analyser to separate out the ions of a selected mass. However, in practise no ion source exist with such properties.

While earlier ion sources mainly was of thermal or spark types the plasma ion source is fairly new. During the early seventies it became evident that it could be possible to sample ions from flames and plasmas even at atmospheric pressure. This would be most advantageous since the temperature in inert gas plasmas would be around 5000-7000 K which would be enough to ionize most elements. Ordinary flames, where temperatures of up to 3000 K could be reached, is simply not hot enough to be able to ionize enough amount of elements in the periodic table. That plasmas had this capability was already known from atomic emission lines observed in the plasma while injecting different elements into it. The potential problems of ion extraction from the plasma seemed formidable however, since the ions could not be analysed until they were in high vacuum. The first attempts in the seventies of combining a plasma (generated by DC instead of a RF-field) and a mass spectrometer was done by sampling the ions from the plasma tail through a 70 um aperture by an electrostatic extraction lens. In order to maintain the high vacuum in the mass analyser the volume following the aperture had to be pumped by a high vacuum pump (1000-2000 lpm) thus removing most of the uncharged atoms and molecules but leaving the ions who were guided by electrostatic lens system further into the mass analyser.

Even though these first experiments (in 1974) showed promise of very good sensitivity and low background between peaks it turned out that the signal was extremely sensitive to the amount of ions in the sample and acceptable spectra was produced only from simple solutions. It was also evident that the degree of ionization was poor for elements having ionization energies above about 9 eV. These problems arose due to a too low effective plasma temperature and a very small fraction of the introduced solution reaching the high-temperature regions of the plasma. The low plasma temperature (around 5000 C) was due to the use of a DC source to generate it although RF-plasmas generating higher temperatures was very well known from ICP-AES.

The discovery that it would be possible to extract ions from plasmas initiated a intensive research starting where the DC-plasma programme had stopped and by 1980 the first successful extraction of ions from an ICP-plasma (that is a plasma generated by inductively coupling from a RF-source) was conducted. Still problems remained having a small interface between plasma and mass-spectrometer limiting the sensitivity. The solution of using a larger aperture seemed first not possible due to the problems in maintaining vacuum and sufficiently low temperatures behind the aperture. These problems were solved by increased cooling of the interface (using water cooling), using a double aperture interface (sampling and skimmer aperture) and increased pumping capacity. Based on this configuration the first commercial ICP-instruments were out on the market in 1983. The instruments today still operate with roughly the same set of parameters as in the start meaning a 10 000 C doughnut formed ICP maintained by a 1-2 kW RF-field with a 27 MHz frequency fed through a load coil to Argon gas flowing through a quarts made torch of Fassel type at flow rates of 12-15 lpm. A picture of the torch and the two cones (sample cone and skimmer cone) are presented in figure 1.

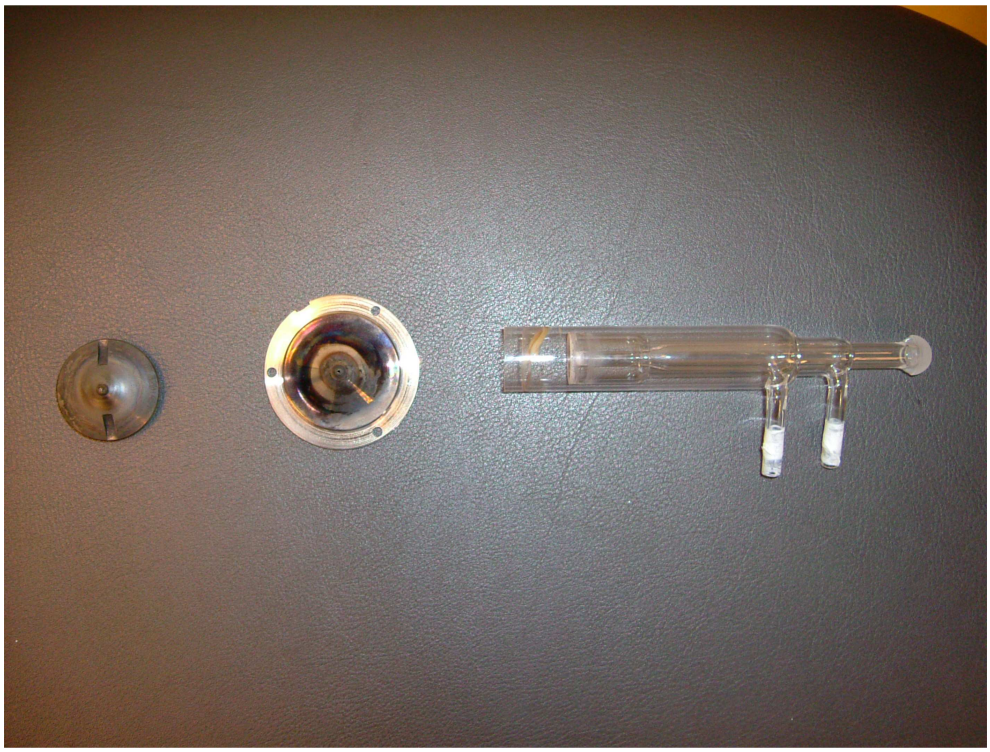

Figure 1
The torch and the two cones separating the plasma from the mass spectrometer.

The solution to be analysed is usually transformed to aerosols and transported to the plasma through the torch where it is volatised, molecules dissociated and atoms excited (for use in ICP-AES) and finally ionised. Typical residence time of atoms in the plasma is in the order of 5 ms.The depth in the central channel of the plasma where ions are sampled via the sampling/skimmer cones to be transported to the mass spectrometer is critical for both sensitivity and the magnitude of interferences from molecular ions. Since the total effect in the plasma is rather low its ability in volatising, dissociating and ionising the incoming sample largely depends on the sample introduction rate and its water and salt content (generally referred as to the matrix load). It is this sensitivity in both plasma geometry coupled to the sample composition and introduction technique which makes the use of ICP-MS a rather complicated issue when it comes to optimizing both for transmission (sensitivity) and interferences.

The source generation from sample introduction to its final ionization may be summarized as in the table below.

Location	State of sample	Event
Sample vessel	Solution	Self aspirating or pumping
Nebuliser	Aerosol droplets	
Spray chamber	Selected droplets	Large diameter droplets rejected
Torch capillary	Droplets	Transport to plasma
Plasma central channel	Droplets	Desolvation
Plasma central channel	Salt particles	Volatilisation
Plasma central channel	Molecular vapour	Dissociation
Plasma central channel	Atoms	Excitation and ionisation
Free space	Atoms and ions	Exit from torch

The mass spectrometer

Once sampled from the plasma the next task for an ICP-MS is to produce a mass-spectrum of the sampled ions. From the plasma temperatures of around 8000-10 000 C ions are mostly single ionised although higher charge states is present. Focusing and transport ion optics in the mass spectrometer is therefore set to select single ionised species. The task of this ion lens system is to form as many ions as possible from the cloud at the rear of the skimmer aperture into an axial beam of circular cross-section at the entrance to the mass analyser.

The mass analyser may be of two three types, a quadropole, a fixed magnetic sector or of time-of-flight type. The quadropole based mass analysers are the most common and may provide mass resolutions down to about 0.5 amu. For higher resolutions (down to 1/10 000 amu) magnetic sectors are used.

The quadropole mass analyser consist of rods of 12-18 mm diameter and about 200 mm long. They act as a mass filter along the axis of which a stable ion path exist for ions of only one mass. Other ions are deflected away from the axis and lost by the action of a combined oscillating RF and DC-field. The transmitted mass is determined by the amplitude of the combined RF and DC potentials and the resolution is determined by their ratio. It is important that the ions experience an adequate number of RF field cycles in order for the system to obtain sufficient resolution. This means that the ion should travel relatively slowly through the rod system and therefore quadropole based mass spectrometers have a very low acceleration voltage (resulting in ion energies of only a few eV). The disadvantage with this is that the ion cloud after the skimmer cone has long time to become dispersed before being drawn into the analyser, this leads to overall low transmission and a relative large risk of mass fractionation (the preferential deflection of lighter ions out from the ion beam). Advantages with the quadropole mass analyser is that the RF and DC fields may be controlled electrically at high speed which therefore permits fast scanning through a complete mass spectrum. The resolution is however limited to about one mass unit prevents identification of interferences.

The magnetic sector mass analyser has been a central part of mass spectrometers since the very first machines were constructed by Aston and co-workers in the beginning of the1920'ies. In determining both the energy and momentum of the ion its mass is uniquely determined. The tools for doing this are the magnetic (momentum) and electric (energy) fields. The magnitude of the deflection of ions in the magnet is governed by the momentum of the ion and the ion path through the magnet is simply determined by

$mv/r = zB$

and since the ion energy gained through acceleration from the ion source is

$1/2\ mv^2 = zV$

With only single charged ions considered and with a constant magnetic field and acceleration voltage the radius will be determined by
$r = \sqrt{(2mV/B^2)}$

Thus it is possible to separate ions of a selected mass by simply selecting a appropriate acceleration voltage and magnetic field strength. Also the whole mass spectrum may be scanned by changing the V and/or B fields.

Since ions of different energy (but possible of the same mass) are turned through different angels an energy dispersive optic device using an electric field is often combined with the magnet. The ion path through this curved plate electrostatic analyser (ESA) is governed by the relation:

$zE = mv^2/R$

Combining with the energy of the ion due to the acceleration voltage ($zV = ½\ mv^2$):

$R = 2V/E$

Thus, in the ESA the ion flight path bends in an arc only depending on acceleration voltage and ESA voltage.

In ICP machines with their relative large spread in initial ion energy the magnet is a necessary part in order to achieve the resolutions required to resolve interferences. If the quadropole mass analyser could provide resolutions of around 300 the magnetic sector ICP-MS instruments may have resolutions greater than 10 000.

The term ‘double focusing’ mass spectrometers are frequently used for the high-resolution ICP-MS instruments. This is because the combined magnetic sector and ESA system focuses both in angle (direction) and energy.

For double focusing instruments mass resolutions of up to 10 000 or more is usually achieved. The ion beam, with a cross-section defined by an entrance slit, will be focused by a sector magnetic field to an image of this slit behind the field where an exit slit can be used for further refinement. From this point of view the magnet has directional focusing properties. The image of the entrance slit, however, can be considerably broadened if the ions have a certain energy spread since the magnet have energy dispersive properties which will blur the image of the entrance slit. Due to the plasma temperature and the ion extraction process the ions of the same mass may still differ in energies of some ten eV meaning that correctional optic must be used to obtain a sharp image of the entrance slit. The most common method is to include a second analyser having energy dispersive properties too, but opposite to that of the magnetic sector. Such an analyser will be an electric sector field which may be a simple cylindrical condenser and is usually named an electrostatic analyser or ESA. It should be pointed out that double focusing conditions can only be realized with specific combinations of the electric and magnetic sector field angels and appropriate geometries.

The magnetic sector ICP-MS instruments have some important properties which makes them different from the simpler quadropole instruments. Firstly the resolution may be changed by simply adjusting the slit widths, from low resolutions of $M/\Delta M$ of about 300 to high resolution of about 10 000 compared to quadropole instruments which have resolutions in the range 300-500 due to a constant peak width (usually between 0.5 and 1 mass unit) over entire mass range (and thus a varying mass resolution). Secondly, the sensitivity for double focusing instruments is generally better than for quadropole instruments due to better transmission and lower background. This is discussed further below. Thirdly, the peak shape may be adjusted by slit and instrument optic settings to obtain flat topped peaks which favour measurements of isotope ratios in single detector instruments. On the other hand the trapezoidal peak shape obtained in sector field instruments means poorer abundance sensitivity (the detection power of a small peak next to a large neighbour peak) than in quadropole instruments for the same mass resolution. Also, the mass scanning rate is faster with quadropoles due to hysteresis problems in the magnet of sector field instruments. However, over small mass ranges (10-30% of the selected central mass position) the sector field instruments may scan by using only variations in the acceleration voltage without using the magnet. Scanning speed may in these cases be of the same magnitude as for quadropole instruments.

As mentioned the sensitivity for sector field instruments is superior to quadropole instruments. The high ion extraction voltage used in sector instruments allows for a better ion focusing and thus a better transmission. The quadropole mass analyser can only handle relatively slow ions and therefore acceleration voltage is low (a few eV compared to several keV in sector instruments). The losses due to thermal diffusion and electrostatic repulsion away from the beam in quadropole instruments are thus more severe. In fact, most of the analyte losses in the entire path from plasma to detector have generally been attributed to

space charge effects in the beam leaving the skimmer cone. Improvements in the extraction lens system behind the skimmer cone for more recent instruments have therefore meant a significant increase in sensitivity. The same phenomena are the reason why heavy ions are less deflected than light ions and therefore show greater transmission. This is generally referred to as the matrix effect, the more the ions present the worse the electrostatic repulsion and the worse the transmission. In practise however the majority of ions present results from the plasma gas and the water in which the sample is usually present in. The matrix effect also includes plasma related phenomena such as lack of ionization energy when supplied by a large amount of energy demanding sample (eg. 2M of an element with high ionization energy such as iodine).

For the average quadropole instrument the transmission is in the order of one ion detected for every 50 000 – 500 000 ions in the plasma while for sector field instruments the transmission may reach one ion for every 500 – 5000 in the plasma. For the sector instruments the losses after the skimmer is relatively small and instead the major loss is in the transfer from plasma to extraction optics (that is through the sampling and skimmer cones) where only some 0.1% of the ions pass.

The second factor which makes sensitivity better for sector instruments is the low background which reaches some 0.2 cps and mass unit compared to 20-50 cps for quadropoles. The difference is mainly due to the photon flux from the plasma which is more easily scattered to the detector in quadropoles than in sector instruments due to the curved flight path in the latter geometry.

The detector

The detectors used to detect the ions in mass spectrometers are usually current measuring Faraday cups for intense ion-beams and/or the more sensitive electron multipliers for direct ion counting in low intensity beams. Sometimes scintillators are used as the ion counting detector instead of the electron multiplier. When measuring high intensity ion beams (several millions of ions per second at the detector) it is not suitable to use ion counting systems due to dead-time problems (described below) and the fact that the ion counting device will be degraded in sensitivity in proportion to the accumulated number of ions hitting the detector. The Faraday detector used instead is simply a metal cup in which the ions strike the inside of and thereby cause secondary electrons to be released. Until the electrons become recaptured by the cup a flow of electric current starts towards the detector. This current constitutes a direct proportional measure of the amount of electrons emitted and thus by the rate of ions entering the cup. The Faraday cup thus delivers a current reading. It is simple and robust and is usually used in situations in which high sensitivity is not required.

The electron multipliers often used for direct ion counting operates just like the photomultiplier tube dynode chain used in NaI(Tl) or other scintillation detectors. The incident ion beam cause two or more electrons to be emitted from the first dynode. These electrons are accelerated towards next dynode and more electrons are emitted etc. In this way an incoming ion will produce some 10^6 electrons at the last dynode. This electron pulse may be treated in ordinary electronic amplifiers and by pulse electronics to be counted as a single event and stored in a multichannel devise.

Figure 2
The detector unit for a PlasmaTrace2 instrument. Shown to the left is the deflection unit and in the central parts the multiplier and the Faraday detector.

The scintillation detector (usually known as the 'Daly' detector) operates by transforming the initial ion beam to secondary electrons at a first photocathode. These electrons are accelerated towards a scintillator and the emitted photons registered by an ordinary photon multiplier.

Isotope ratio and ultra trace measurements

Isotope ratios

The considerations of instability when using ICP-MS instruments for isotope ratio measurements include the sample introduction system, the plasma flickering, instrumental background and interferences as well as detector dead time and general construction.

Two of the most fundamental characteristics of any spectrometer are its resolution and sensitivity. As resolution is increased, transmission and thereby sensitivity is decreased. Accurate measurements of isotope ratios will be limited by overlapping of adjacent peaks which is particularly important to consider for minor isotopes (such as measurement of ^{234}U which is next to the much more abundant ^{235}U). Obviously, when dealing with isotope ratios of trace amounts a compromise may be necessary between resolution and transmission. In most applications where environmental levels of radioisotopes are measured the need to maximize transmission is however the most important priority.

In practise there are two different ways of obtaining isotope ratio measurements when using single detector instruments, scanning and peak jumping. In the scanning mode a spectral

region is scanned at a uniform rate using a multichannel analyser in the time-based mode. A number of scans is simply summed and treated as a single spectrum. The principal advantage of this approach is that the shape of the peaks is recorded. The disadvantage is that a significant amount of data acquisition time is spent on scanning the regions between peaks and that the same amount of time is spent on intense as well as weak peaks. Ratios of peaks are then calculated from the areas under the peaks and it is therefore important that analyser channels used to calculate the peak area sample the same fraction of each peak. The use of a large number of channels per mass unit (30-50) may therefore be useful. If too few channels per mass unit is used (less than 10) the accuracy and precision is degraded.

In the peak jumping mode the instrument is programmed to step to specific mass values. In this way only data for the specific peaks of interest is collected and less time is spent on data acquisition between peaks (this fraction may of course be included in the jump mode as well). Due to the overall signal instability in ICP instruments peak positions and peak shape is not constant with time. Therefore it is common to scan the individual peaks instead of just measuring the peak top intensity.

The advantage with magnetic sector double focusing instruments is that flat topped peaks may be achieved by adjusting slits and transmission optics. In doing this maximum time is spent at maximum signal intensities and thus the statistical part of uncertainty in the isotope ratio determination is minimized. In quadropole instruments this is not possible due to the rounded or triangular shape of the peaks at all instrumental settings. Hopping between peak top values therefore require the instrument to be absolutely stable and allows for only very small drift in spectra position. For double focusing instruments the limitation therefore is the ‘ripple’ at the peak top which is due to the overall signal transport variation from sample introduction, aerosol generation, plasma flickering etc. In thermal ionization mass spectrometry (TIMS) this peak ‘ripple’ is very low (typical in the ppm range) due to an almost completely stable ion beam and isotope ratio measurements is thus mainly limited by counting statistics at ultra trace measurements.

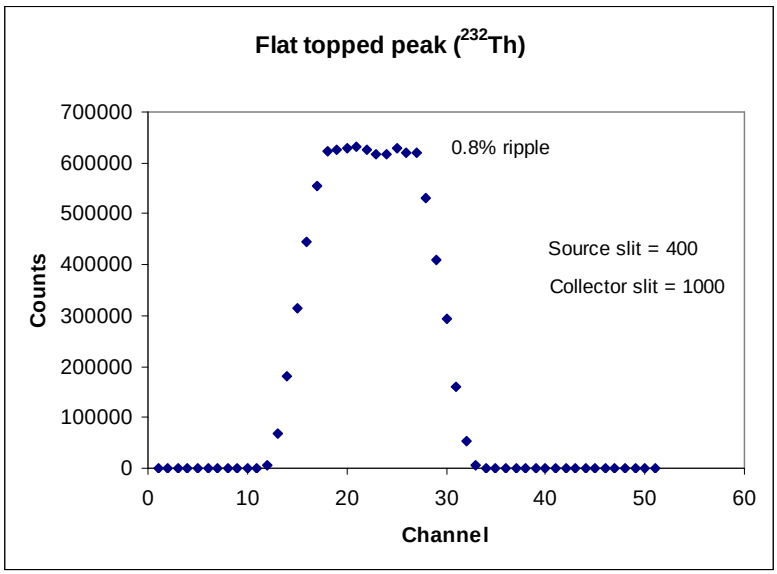

Figure 3
Peak-shape for a magnetic sector field instrument (PlasmaTrace2).

For magnetic sector instruments it may be concluded that the major effort to improve isotope ratio measurements should be spent on *both* the sample introduction system and the peak flatness while for quadropole instruments the major improvement is to be made at the sample introduction system.

A common problem to all event counting electronic systems are their inherent *dead time* or their inactive time following the registration of an event. Just as in radiometric counting systems where the preamplifiers, ADC's etc. in gamma and alpha spectrometry may show problems with dead time at high counting rates the same problem occur in mass spectrometry. The problem is of considerable importance when determining accurate isotope ratios between high and low abundance isotopes, such as $^{234}U/^{238}U$ ratios. In an ordinary sample with some ppb of natural uranium the count rate for ^{234}U is only a few hundred to some thousand cps while for ^{238}U it may be in the order of millions cps. Since the total dead time of the counting system is in the order of tens of nanoseconds the risk of underestimating the ^{238}U concentration is obvious. Although there are ways of adjusting the hardware to better accept high count rates the common way of correcting for dead time is by measuring it and then apply a mathematical expression which gives the true count rate. The expression to use depends on if the system is paralysable or not. The measurement may be performed by using certified reference materials (CRM) having well known isotope ratios of some low and high abundance isotope, for instance ^{235}U and ^{238}U. Typically two or more CRM's with different $^{235}U/^{238}U$ values are used and the measured ratios corrected for an assumed dead time is plotted versus the applied dead time. The appropriate dead time is the value when all CRM's show correct ratio. The data has however first to be corrected for mass bias.

The mass bias of isotopes means that isotopes of different mass are not carried through the mass spectrometer with equal efficiency. One example is the preferential evaporation of lighter isotopes from the filament in TIMS. In ICP-MS the fractionation is mainly opposite in that the lighter isotopes are easier removed from the ion beam due to electrostatic repulsion, mainly due to the space charge effects introduced where the ion cloud is the densest which is in the region of the skimmer cone. This mass fractionation is thus matrix dependent. Other reasons, such as the mass scanning method, detector response or the fringing fields in the vicinity of the quadropole also influences the mass bias.. The mass bias may be corrected for by using CRM's. Typically the mass bias ranges around some 0.1-0.5% per mass unit for most ICP-MS instruments.

Considering the above mentioned corrections and other factors such as instrument background, linearity and possible interferences makes it possible to perform isotope ratio measurements with a precision of down to 0.1% (RSD) with double focusing instruments and about 0.5% for quadropole instruments provided the counting statistics are not adding to the uncertainty. For multicollector ICP-MS or TIMS instruments isotope ratios may be determined down to 0.001% RSD.

Ultra trace measurements

With focused efforts to lower instrument background and maximise sample introduction efficiency and transmission it is theoretically possible to quantify sub-femtogram quantities of an isotope in a sample. In doing this it is absolutely necessary to remove any trace constituents that may cause interferences at the mass position of interest (eg. UH^+ at mass 239 in analysing for plutonium). Unfortunately there is a wide spread view that with the best instruments, having an overall absolute sensitivity of about one count per 500 atoms,

technology is so outstanding that chemical separation methods is no longer necessary. The truth is however the opposite in that chemical separations are required even more in order to fully take advantage of the high sensitivity offered by these instruments. This also holds for multicollector ICP-MS instruments. The reason is simply that the abundance sensitivity (or simply the spill-over of ions from one mass to the neighbour mass) in any ICP-MS in high transmission mode is not good enough to permit more than about 10^4-10^6 counts at the neighbouring masses of the analyte before (uncertain) corrections for the spill-over fraction must be applied. In the analysis of plutonium and neptunium it is almost entirely the amount of remaining uranium in the purified sample which determines the detection limit. But it may also be due to more complex interferences like $^{204}Pb^{35}Cl^+$ just to mention one possibility. For isotopes like ^{99}Tc the complete removal of ruthenium (due to ^{99}Ru) and the major amounts of Mo (due to the spill-over from ^{98}Mo and ^{100}Mo) is necessary.

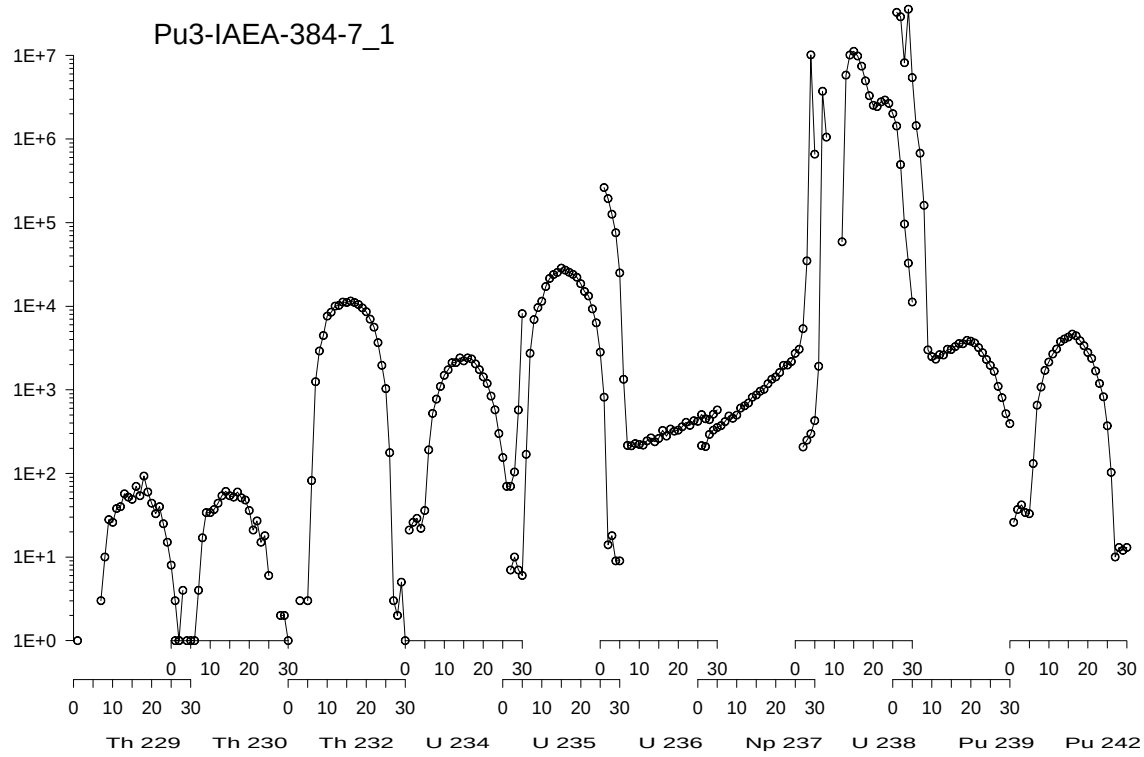

Figure 4
The spill-over, or abundance sensitivity, shown for a Pu-sample where the uranium has not been sufficiently removed. The huge ^{238}U peak prevents accurate determination of both ^{239}Pu and ^{237}Np.

The chemical separation techniques required to reliably measure the ultra low levels may be similar to the ones used for radiometric measurements but purity and volume of chemical reagents should be considered. In general it is far easier to minimize the amount of reagents than to increase their purity. It could be mentioned that in the extreme end sample purification may be performed using ion exchange consisting of only one bead of resin and a few microlitres of acid.

Other factors worth considering when doing general trace determinations are the risk of sample to sample contamination and thus the wash-out from the mass spectrometer system before next sample, the risk of airborne contamination to the sample introduction system (avoided by putting it into an laminar flow hood) and the purity of yield tracers for the isotope dilution purification (minimized by minimising the tracer amount added to the sample) as well as the need to include procedure blanks processed simultaneously as the real samples.

The need to include blank samples in low-level ICP-MS analysis should be taken as a standard procedure since it increases the credibility even though the operator is convinced that the blank levels are insignificant. An example of the levels of blank contribution when performing low-level uranium analysis (some tens of μBq) in vegetation samples is shown in figure 5.

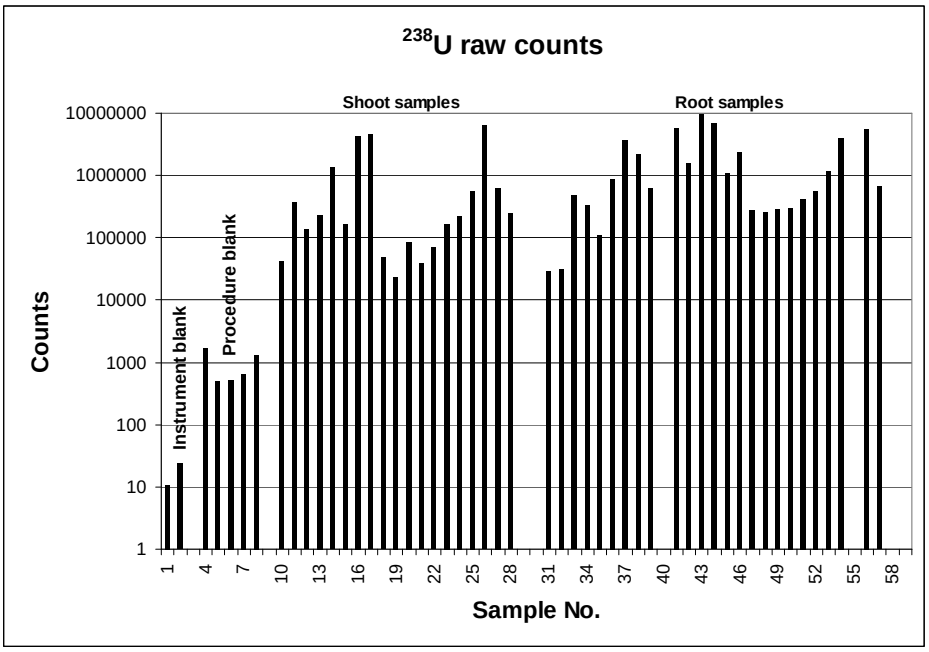

Figure 5
Diagram showing relative contribution of instrument blank, process blank (zero-material sample, only chemicals) and samples when analysing μBq-levels of uranium.

A few practical tips when working with an ICP-MS

This text is in no way meant to replace the instructions manual provided with the users instrument. Assuming that the recommended regular maintenance service and exchange of oil filters, extraction slits etc. are performed the suggestions below are merely meant to assist during daily operation. Neither is it aimed to be a fully comprehensive instruction, but is intended for users as a base for discussion and exchange of experiences to ease the daily work.

Sample analysis:

Some of the problems when measuring ultra low levels of Pu-isotopes with commercial ICP-MS instruments are the relatively low abundance sensitivity, the risk of interferences from polyatomic species, blanks, background and sensitivity. In order to minimize the problems, both instrumental settings as well as sample conditions may be optimised. Tailing from interfering peaks may be restricted by attempting to change the peak shape by hardware settings, polyatomic species may be partly removed by desolvating equipment and chemical separations and sensitivity may be improved by a suitable sample inlet system

A problem of particular importance when using ICP-MS for ultra low level measurements of any element is the relatively poor abundance sensitivity. Correction for tailing from adjacent peaks onto a given mass is commonly done either by subtracting values interpolated from signals measured at half-mass positions from the peak to be corrected, or by applying a predetermined correction value. Disadvantages with the first method is that the peak is subtracted for its own tailing and that the tailing is assumed to be linear which it is not. Also with the second method care needs to be taken as how to apply the obtained value. For instance, if it is a value obtained over the integrated peak it is important to use the same mass interval during the correction as during the separate measurement of the abundance sensitivity. Values of abundance sensitivity may refer to the peak position or over the whole peak base region. In the latter case measured abundance sensitivity will be larger than the former. Thus, it is difficult to accurately perform corrections for peak tailing which is necessary at ultra low level measurements unless uranium decontamination may be held sufficiently low.

Once the abundance sensitivity has been determined it is important that the peak tail profile is fairly constant over the narrow mass range of interest (eg. between mass 238 and 242 for instance) and that it is independent of the ion beam intensity. This has tested in several experiments and found to be reasonably true.

One possible way to improve the abundance sensitivity in ICP-MS instruments is by increasing the resolution of the system. This however also reduces the sensitivity. For sector field ICP-MS instruments the possibility of obtaining flat topped peaks by adjusting the source slit width is an advantage in the analysis of low concentrations simply because peak hopping between the flat region is safer than a similar manoeuvre for rounded peaks (as in quadrupole ICP-MS) if drift in mass calibration changes with time. In the figure below a uranium spectra from CRM 112a has been obtained both by open slits (rounded peaks) and by partly closed source slit (flat top peak).

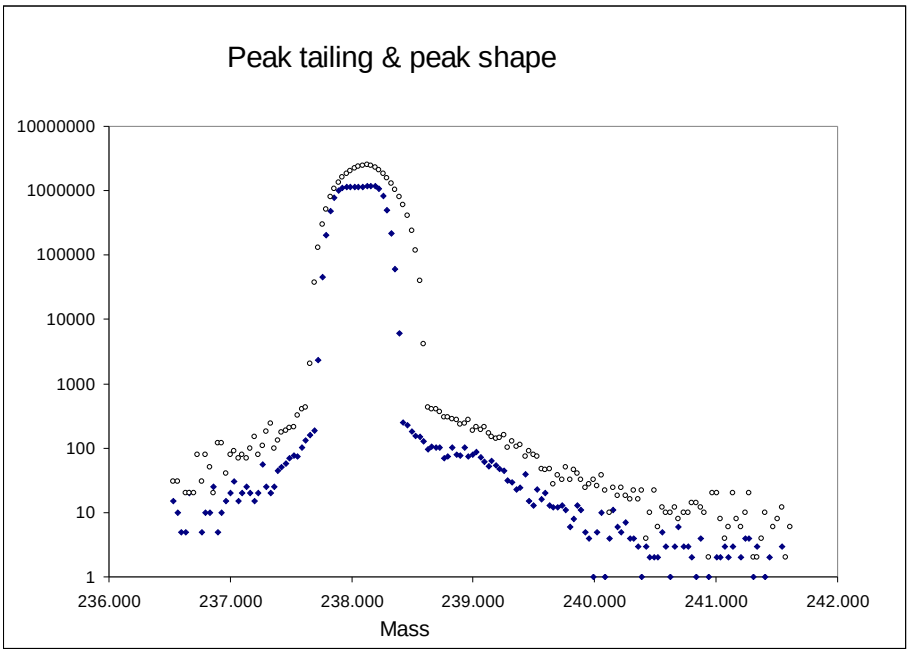

Figure 1: Mass spectra of ^{238}U with fully open slits (rounded peak) and partly closed source slit (flat top peak)

Apart from the peak tailing, which mainly is of instrumental origin, also the UH^+ interference at mass 239 needs to be considered. The mass resolution needed to resolve this peak from ^{239}Pu is about 37 000 which therfore not is practically possible. During ultra low level measurements it is also not possible to increases resolution due to loss in transmission. Since the UH^+ interference depends on the amount of hydrogen (water) present in the plasma the magnitude of the peak depends on several factors such as nebuliser flow rate, sample uptake rate and sample introduction methods. Among these the sample introduction method is a very important factor in affecting the hydride generation

There are a number of potential interferences apart from the UH^+ that may be of importance at trace level determination of plutonium isotopes. These may originate from combinations of elements present in the plasma gas, sample and solute atoms. Even though they may not be of great importance when analysing gram amounts of soil and sediments where total Pu levels are in the pg to ng range care must be taken either when ultra low levels are analysed and/or when high precision isotopic ratio information is of importance. Even though the ratio of plutonium to interfering elements may be the same regardless if large or small samples are analysed the trace amount of Pb, Hg, Tl and Bi present in the laboratory environment poses a larger risk to small samples and must be considered even though separation of Pu takes place. Since it is difficult to remove elements originating from the plasma gas (Ar and trace rare gases) focus is therefore mainly directed to remove constituents in the sample and solute. Examples of interfering elements for the mass range 239 to 242 is presented in the table below but also other potential interferences may be present in specific cases and this necessitates careful analysis of the risks given during any sample and sample processing procedure including blank samples to be analysed in an identical manner as real samples. Another alternative in identifying the influence of polyatomic interferences in a sample is to use a higher resolution or to mass calibrate very carefully and observe potential peak shifts but this is seldomly possible with ultra trace Pu analysis since the peak shape don't permit

accurate mass determination. Using higher resolution is neither an alternative due to the loss in transmission

Polyatomic interference	m/z
Interferes with 239Pu	
$^{204}Pb^{35}Cl$	238.9419
$^{203}Tl^{36}Ar$	238.9399
$^{204}Hg^{35}Cl$	238.9423
$^{202}Hg^{37}Cl$	238.9365
$^{201}Hg^{38}Cl$	238.9330
$^{199}Hg^{40}Ar$	238.9306
Interferes with 240Pu	
$^{204}Pb^{36}Ar$	239.9341
$^{205}Tl^{35}Cl$	239.9433
$^{203}Tl^{37}Cl$	239.9382
$^{204}Hg^{36}Ar$	239.9410
$^{202}Hg^{38}Ar$	239.9334
$^{200}Hg^{40}Ar$	239.9307
Interferes with 241Pu	
$^{206}Pb^{35}Cl$	240.9433
$^{204}Pb^{37}Cl$	240.9389
$^{205}Tl^{36}Ar$	240.9420
$^{203}Tl^{38}Ar$	240.9351
$^{204}Hg^{37}Cl$	240.9394
$^{201}Hg^{40}Ar$	240.9327
Interferes with 242Pu	
$^{207}Pb3^{5}Cl$	241.9448
$^{206}Pb^{36}Ar$	241.9419
$^{205}Tl^{37}Cl$	241.9397
$^{204}Pb^{38}Ar$	241.9358
$^{204}Hg^{38}Ar$	241.9362
$^{202}Hg^{40}Ar$	241.9330

Table 1: Polyatomic intereferences from some trace metals with argon and chlorine.

Optimum use of sample:

Since the analysis of very low levels of plutonium often means having limited amount of sample it is important to make the best use of what is available. In normal day use of ICP-MS instruments they are often tuned by adjusting torch position, gas flows and some optical settings to gain maximum sensitivity with respect to counts per second per concentration unit in tuning solution. Less frequent does the tuning address the maximum use of the sample, which is more important when a limited amount of it is available. Since typically only some 5-15% of the liquid reaching the nebuliser is transported to the plasma it is important to consider what fraction is drained away. Simple experiments where both uptake and drain rates, as well as concentration in drain, are easy to do and may improve sample use by a factor of 2-10. Typically, best use of the sample is done at very low flow rates which means

that in ultra trace analysis also the instrument background needs to be considered since analysis time will be longer for a given sample volume.

The higher absolute efficiency at lower uptake rates is probably a combination of better aerosol and transport through the spray chamber as well as ionisation of the element in the plasma (less energy is spent per time unit on the water entering the plasma). Another effect reducing the efficiency at higher feed rates (although rather unimportant) is the increased rate of oxide formation, which probably is due to lowering of the plasma temperature at increased feed rates.

General considerations in sample analysis with ICP-MS

One of the main obstacles when working with ICP-MS and analysis of unknown samples is, non-spectroscopic,matrix induced interferences causing either signal enhancement or suppression. The mechanisms for these interferences are still poorly understood, and below are a few suggestions given on how to limit the influence of some of them.

It is good to have some idea of the ionic strength (approximate concentration is good enough) of the sample. As ions traverse through the plasma it cools off, and with increasing ionic strength follows a decreasing plasma temperature. The effect of mass discrimination is increased by a decreased plasma temperature. Also, as the ions have different ionization potentials, a colder plasma may not be sufficient to ionize *e.g.* Zn (9.4 eV) or other elements with high ionization potentials to the same extent as in the standard solution. To find out the approximate sample constituents sometimes another instrument can be used, *e.g.* an ICP-OES (optical emission spectrometer), however analysing a well diluted sample also gives an idea of the composition and thereafter dilution to a suitable level can be performed.

As a rule of thumb it may be worth trying to look at the total Na and Ca content because in natural samples these ions are often the major contributors to the ionic strength. A practical upper limit for total [Na^+] is approximately 1000 ppm (0.1%), and for total [Ca^{2+}] ~400-500 ppm. With cations comes anions, and high levels of Na^+ and/or Ca^{2+} is often indicative of high concentrations of Cl^-, preventing measurements of *e.g.* ^{75}As ($^{40}Ar^{35}Cl$) and ^{51}V ($^{35}Cl^{16}O$) and increasing the risk of polyatomic interferences at masses 239-243 due to chloride species of Pb, Bi and Tl. If dilution is not possible, a match between the sample and standard matrix is required for quantitative analyses.

An internal standard (I.S.) is necessary to correct for non-spectral matrix disturbances. Indium is often used since it is not naturally present in the environment, but other elements can be used as well *e.g.* U, Tl, Lu, it depends on the element of interest as well as sample composition. Choosing an I.S. in the same mass range as the elements of interest limits the effects of mass bias induced error.

During operation an I.S. can be used as a quick reference of the instrument operating performance. If the intensity of the I.S. suddenly drops it can be a indicative of a sample with high ionic strength. This can be verified by checking the Na^+ response. Sometimes the response comes back if the following samples are less saline. However, keep in mind that there will be memory effects from a sample with high ionic strength (salt content) and the instrument may need to be washed for some time before the next sample is analysed. The memory effect of $^{40}Ar^{35}Cl$ on the As response can sometimes last for several hours.

During operation and especially if analysing samples with a high salt content, salt deposited on the orifice of the cones eventually cause a reduction of the entrance diameter. This changes the response in a non-linear way, and relative to the ^{115}In (I.S.) response this may give an underestimated response from lighter elements whereas the response from heavier elements may be overestimated.

Use of an I.S. is also indicative of how the sample introduction system operates. If an obstacle in the nebulizer suddenly obstructs the flow, the I.S. signal is dramatically decreased. Often the decreased signal is also unstable, *i.e.* an increased RSD value is a warning sign that something went wrong during the analysis. An unusually high RSD value can also be indicative of a memory effect. When analysing samples it is inevitable that a high concentration of some element is entered into the instrument.

Digested solid samples often contain particles that have not completely dissolved. To avoid unnecessary clogging when analysing samples that are not suitable for filtration, centrifugation of the sample often does the trick.

Cleaning the sample introduction system:

Remove the sample and skimmer cones. Place them over night in hot water with some soap. In the morning use a Cleenex tissue or some other wipe and try to remove the loose residue on the cones. A round cocktail stick can be used gently (Ni is quite soft) to clean the holes in the cones. Rinse the cones with water, MQ-water and etanol and dry them with *e.g.* high pressure air or nitrogen. Avoid unnecessary finger contact with the cleaned cones. Cover the installation tool with a Cleenex tissue before placing the cones on it to avoid direct contact between the tool and the cones during installation.

If biological samples were analysed such as urine or blood/serum, proteins are deposited on the torch. When cleaning the torch it is therefore good to start by flushing it with hot water. The torch can thereafter be left soaking over night in 5-10 % HNO_3. In the morning rinse the torch with MQ-water and ethanol and dry it the same way as with the cones. Avoid touching it as much as possible, especially the parts that get hot during operation.

The spray chamber may be cleaned with hot water, soap, ethanol or acid, depending on the samples that have been analysed, but cleaning of the spray chamber is not needed as often as cleaning the cones. The cleaning procedure should however, always end with rinsing the spray chamber with MQ-water.

If a particle is stuck in the nebulizer or just for regular cleaning, an ultrasonic bath can be used. If this does not help try back flushing (water stream vacuum) the nebulizer with MQ-water, ~10% HNO_3, ethanol, or soap water. To avoid unnecessary chemical reactions always rinse with water between different solvents. Soaking the nebulizer over night may ease the process of cleaning. Always rinse with the HNO_3 solution and MQ-water before installation.

The auto sampler tubing may also need to be cleaned. Cleaning the tubing should be performed off line using the peristaltic pump, and the solution should always go to waste instead of into the nebulizer. Various acidic and alkaline solutions can be used as well as organic solvents such as ethanol (10-50%). Choose the cleaning solution depending on the samples that have passed through the tube. To avoid unnecessary chemical reactions always

rinse with water between different solvents, and always end with the rinse solution used when operating the instrument.

When the cones are freshly cleaned the Ni-blanks are always high. To reduce the blank values the Nearshore seawater reference material CASS-4, diluted 1:10 can be allowed through the system for a few minutes after start. This covers the cones with a thin layer of salt and the blank values are decreased. Also for this procedure, let a plug of MQ-water through the system both before and after CASS-4 treatment.

The cleaning frequency of cones and torch are dependent on the samples that were analysed. If sea water or blood samples are analysed, cleaning may have to be performed daily. If the samples are mainly tap water or similar low ionic strength water samples cleaning may not be required for much longer time. Normally, the cones need the most frequent cleaning followed by the auto sampler tubing and torch.

Literature

There are a number of good publications and books covering most aspects of ICP-MS and mass spectrometry in general. For the reader who wishes to know more about the subject the following general literature is recommended.

1. Applications of Inductively Coupled Plasma Mass Spectrometry, ed. A. R. Date and A. L. Gray, Blackie, Glasgow, 1989.

2. Handbook of inductively coupled plasma mass spectrometry, ed. K. E. Jarvis, A. L. Gray, and R. S. Houk, Blackie, Glasgow, 1992.

3. Inductively coupled plasmas in analytical atomic spectrometry, ed. A. Montaser and D. W. Golightly, VCH, New York, 1992.

4. Inductively coupled plasma mass spectrometry, ed. A. Montaser, Wiley, New York, 1998.

5. Plasma source mass spectrometry : new developments and applications, ed. G. Holland and S. D. Tanner, Royal Society of Chemistry, Cambridge, 1999.

6. A beginners guide to ICP-MS by Robert Thomas covering most aspects may be found at: http://scientificsolutions1.com/icpmstutorial.htm

Training course in isotope ratio measurements of Pu and U at low levels using ICP-MS

This training course is directed towards students, scientists or other scientific personnel who have an interest or need to perform mass spectrometric measurements of plutonium and/or uranium isotopes using ICP-MS. The course is primarily aimed at those having only limited experience in ICP-MS but also trained users are welcome. Since the course covers the necessary radiochemical purifications needed to perform low level measurements it is an advantage if the participant has some knowledge in this field.

The duration of the course is adjustable but is estimated to be 2-4 days. Maximum number of participants is 4. The present training course is set up for the PlasmaTrace 2 sector ICP-MS at Risoe National Laboratory in Denmark.

Experiment 1 – Tuning of mass spectrometer system:

The tuning of the system means optimising the set-up with respect to sensitivity, stability etc. In this experiment we use a cooled cyclonic spray chamber and a ^{238}U solution (1 ppb). While performing the adjustments below observe sensitivity and the UO^+/U ratio.

- Adjust auxiliary and nebuliser gas flows.
- Adjust torch position.
- Go through the other optical settings and become acquainted with them. Remember to write down the original settings before adjusting them.
- Observe the useful concentration range for the multiplier and Faraday detector respectively by measuring 1 and 10 ppb ^{238}U solutions.

Experiment 2 - Sample introduction systems:

Since different types of sample introduction systems usually are available at different laboratories it is important to become acquainted with them and become aware of advantages and disadvantages. In this experiment we use three different systems – a cooled cyclonic spray chamber (try also with the cooling stopped), an ultra sonic nebuliser with desolvating system and again a cyclonic spray chamber but now heated and combined with a multipass cooler. After having mounted the different systems, optimise in the same way as in experiment 1 above. It is necessary to perform instrument tuning when switching between the different sample introduction systems.

- Compare oxide (UO^+/U) and hydride (UH^+/U) formation between the different sample inlet systems.

- Compare sensitivity (count rate per ppb in solution) as a function of sample uptake rate.

- Compare absolute sensitivity (count rate per atoms delivery rate to plasma) as a function of sample uptake rate (combine this test with the previous).

- Perform signal and isotope ratio stability test using a standard uranium solution having a well known $^{235}U/^{238}U$ atom ratio.

- Use a 5 ppb U-solution and study memory effects by measuring the residual signal after different amount of aspirated 1%, 2% and 5% HNO_3 respectively.

Experiment 3 – Interferences:

Use the cyclonic spraychamber and the USN and wash carefully with 2% HNO_3 before this experiment.

- Measure the 'normal' background at masses 235-243 using only 2% HNO_3.
- Measure signal count rates at masses 235-243 using a 2ppm Pb solution in 2% HNO_3.
- Repeat the measurement after adding 0.5 ml concentrated HCl to the solution.

How much average soil is needed to provide a 10ml aqueous sample with a 2 ppm Pb concentration? If using a 10g soil sample for Pu analysis how much of the Pb needs to be removed?

- Determine the UH+/U ratio for the two sample introduction systems. How should this be measured?

How much uranium may be tolerated in the sample if a 1mBq ^{239}Pu or 1mBq ^{237}Np is to be measured with less than 5% contribution from the ^{238}U?

Experiment 4 - Instrument parameter set-up and abundance sensitivity:

Perhaps the most serious problem in using sector field ICP-MS instruments for radioisotopes of uranium and plutonium is the relatively poor abundance sensitivity (peak tailing). The influence of peak tailing on neighbouring peaks may be partly adjusted by instrument settings. When analysing for isotope ratios also settings like dwell time and sweep frequency may influence precision. The measured ratio is also to be corrected for detector dead time and mass fractionation.

- Measure abundance sensitivity (signal ratio at mass 237 to 238) and transmission for different source slit widths with fixed collector slit width using a 1ppb ^{238}U solution. Try to obtain flat topped peaks.

- Perform $^{235}U/^{238}U$ ratio determinations on a standard U-solution with varying dwell time but with constant total count time per mass.

- Perform $^{235}U/^{238}U$ ratio determinations with solutions having 0.1-10 ppb uranium and try to determine detector dead time.

- Use a certified $^{235}U/^{238}U$ solution (U500) to determine mass fractionation.

Experiment 5 - Radiochemistry & ICP-MS:

Perform an ordinary separation of Pu from 5g of Baltic Sea sediment, split the final solution in two equal parts. Analyse one part directly for Pu-isotopes and ^{238}U and perform a micro column clean-up (details given during the course) of the other part of the solution before analysis in the same way.

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Abstract

This text is meant as a guide for those who wishes to approach the field of ICP mass spectrometry for one purpose or another. In principle any mass spectrometer consists of three parts: An ion source, a mass analyser and a detector. These three parts will be treated separately in the text before focusing on the specific issues concerning ultra trace measurements and isotope ratios of radioisotopes. The text includes some general considerations with practical tips which are useful to the novel user when doing sample analysis with ICP-MS. It also includes a short training course consisting of five exercises.

Key words ICP-MS, Mass spectrometry, training course, isotope ratio measurements

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